

Glycerol transformations on polysaccharide derived mesoporous materials

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Abstract

New polysaccharide based solid acids are excellent catalysts for selective chemical transformations of glycerol. Reasonable selectivities to mono-, di- and triacetylated glycerols can be obtained by controlled microwave activation of glycerol–acetic and solid acid mixtures. Etherifications of glycerol using a range of alcohols have also been achieved and with a degree of selectivity to both 1- and 2-positions. The use of the Starbon[®] material as a support for palladium further extends the range of heterogeneous catalysed chemistry to the selective oxidations of glycerol to both glycolic and oxalic acids. In all of the reactions, the catalysts can be easily recovered and reused with only a small loss in activity.
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1. Introduction

Glycerol is a by-product of biodiesel production from renewable triglycerides and is becoming available in very large quantities in several regions of the world. In order to deal with the major surplus of glycerol and build on the “green” credentials of the compound, we should develop new and innovative greener catalytic processes to transform the glycerol into high-added value products [1–3].

One interesting transformation of glycerol is esterification with acetic acid or transesterification with methyl acetate to obtain glycerol triacetate, also known as triacetin [4–6]. Triacetin is an industrially available product produced in large quantities. In general, glycerol acetates can be employed as fuel additives as they improve the cold and viscosity properties of liquid fuels (including biodiesel) and also as antiknock additives for gasoline [4–6].

Mono- and diglycerides and their derivatives have also a wide range of different applications including emulsifiers in food [7], pharmaceuticals [8,9] and especially in personal care products [10–12]. The mono- and diglycerides are generally

obtained (1) after hydrolysis of glycerides, (2) transesterification of glycerol with fatty acid methyl esters (FAME) or (3) the esterification of glycerol with (fatty) acids. In order to decrease the temperature of reaction and improve the reaction kinetics for the esterification of glycerol, an acid catalyst stronger than a fatty acid is usually employed (e.g. sulfuric acid, organic sulfonic acids, etc.). Only a few reports have been found dealing with solid acid catalysts including zeolites and silica supported heteropolyacids [1–3,13,14].

Another well-studied transformation is the oxidation of glycerol. Following the work from Prati and Rossi [15], many reports can be found on the oxidation of glycerol to give glyceric and glycolic acids as major products with minor quantities of tartronic and oxalic acids [16–18].

We have recently reported the preparation of a new family of mesoporous carbonaceous materials derived from renewable bio-resources denoted as Starbon[®]. Starbon[®] acids were proved to have excellent activities and selectivities in different acid catalysed reactions including the esterification of various organic acids in water [19–21]. We have also prepared Pd nanoparticles supported on Starbon[®] and reported their use in various C–C coupling reactions [22]. We report here, for the first time, a range of transformations of glycerol performed under microwave conditions employing Starbon[®] derived materials.

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2. Experimental

2.1. Materials preparation

The sulphonated Starbon[®] material (Starbon[®]-400-SO₃H) was prepared as previously reported. [19–21,23] The SO₃H loading in the Starbon[®] acid is ca. 0.5 mmol g⁻¹. The Starbon[®] supported palladium material was prepared as follows: Starbon[®]-400 (0.3 g) was stirred with a solution of palladium acetate (10% by weight) in 5 mL of acetone. The resultant mixture was heated under microwave irradiation for 10 min at 140 °C at 200 W (maximum power output). The solid was then filtered, washed with acetone and dried in the oven at 100 °C for 12 h. The Pd content was found to be 9.2% Pd (obtained by elemental analysis). Sulfonated silica (SiO₂-SO₃H) was synthesized as follows: a HMS material [24] was stirred in a 3-mercaptopropyltrimethoxysilane solution in toluene (under reflux) overnight. The solid was filtered off, washed with toluene and then oxidised with hydrogen peroxide (30%, v/v) at room temperature for 6 h. The resulting material was then filtered off, washed with distilled water and dried overnight in the oven (70 °C) prior to its use in the catalytic reaction. Diffuse reflectance infrared Fourier-transform spectra (DRIFTS) and TG profiles confirmed the presence of the SO₃H groups on the silica. The SO₃H loading was around 0.8–0.9 mmol g⁻¹. Zeolite beta (beta-25, SiO₂/Al₂O₃ 12.5 ratio) was purchased from Zeolyst and activated at 500 °C prior to its use as catalyst in the different reactions. *para*-Toluene sulfonic acid (*p*-TSA, Sigma–Aldrich 98%) was used as purchased. Mono- (Avocado, tech.), di- (Fluka) and triacetin (Avocado, 99%) in the esterification and glycolic and oxalic acids (Avocado, 98%) in the oxidation reaction were used as analytical standards to calculate the response factors.

Microwave experiments were carried out in a CEM-DISCOVER model with PC control and monitored by sampling aliquots of reaction mixture that were subsequently analysed by GC/GC–MS using an Agilent 6890N GC model equipped with a 7683B series autosampler fitted with a DB-5 capillary column and an FID detector. Experiments were conducted on a closed vessel (pressure controlled) under continuous stirring. The microwave method was generally power controlled. The samples were irradiated with the maximum power output (ranging from 100 to 300 W) depending on the reaction investigated. Reaction products were also identified and confirmed by ¹H NMR using a JEOL 400 spectrometer operating at 400.13 MHz. Chemical shifts were calibrated using the internal SiMe₄ resonance.

2.2. Catalyst testing

Glycerol (Sigma–Aldrich, 99.5%) was employed in the various investigated reactions. In a typical esterification reaction, 10 mmol glycerol, 30 mmol acetic acid and the catalyst (0.1–0.2 g) were placed in a microwave tube and irradiated with microwaves under continuous stirring for the desired period of time. The resultant mixture was then filtered off and extracted using ethyl acetate and analysed by GC and

GC–MS. The products mono-, di- and triacetin were identified and their response factors were determined with respect to the starting material from GC analysis using known compounds in calibration mixtures of specified compositions. In the etherification reaction, 2 mmol glycerol and 6 mmol alcohol were microwaved with the catalyst, under continuous stirring, at 300 W (maximum power output) for a short period of time (5–15 min). The resulting mixture was extracted with ethyl acetate, filtered off and analysed by GC, GC–MS and ¹H NMR. Reaction products were mixtures of 1- and 2-monoglycerol ethers together with traces of diethers. Finally, in the oxidation reaction, the 10 wt% Starbon[®] supported Pd material was added to a mixture of 1 mmol glycerol and 4 mmol H₂O₂ and microwaved for some time. The resulting mixture was extracted with ethyl acetate, filtered off and analysed by GC and GC–MS. The main products (glycolic and oxalic acids) were identified and their response factors were determined with respect to the starting material from GC analysis using the pure compounds in calibration mixtures of specified compositions. Minor quantities (<5%) of glyceric and tartronic acids were also detected in the reaction mixture.

3. Results and discussion

3.1. Glycerol esterification

Starbon[®] acids were tested in the esterification of glycerol with acetic acid under microwave irradiation to give mono-, di- and triacetyl glycerols (Figs. 1–3). Quantitative glycerol conversion was observed in all examples. A maximum selectivity of ca. 60–75% was obtained for the mono-, the di- or the triacetyl glycerol, depending on the reaction conditions. A glycerol:acetic acid 1:1 ratio was most favourable for the preparation of monoacetyl glycerol (Fig. 1). 1:3 and 1:6

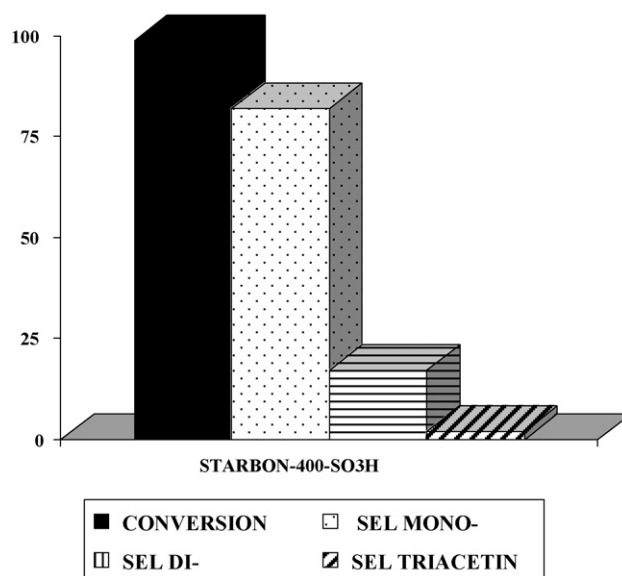


Fig. 1. Optimised preparation of monoacetyl glycerol from the esterification of glycerol with acetic acid. Reaction conditions: 10 mmol glycerol, 10 mmol acetic acid, 100 W, 100 °C, 10 min, 0.1 g Starbon[®]-400-SO₃H.

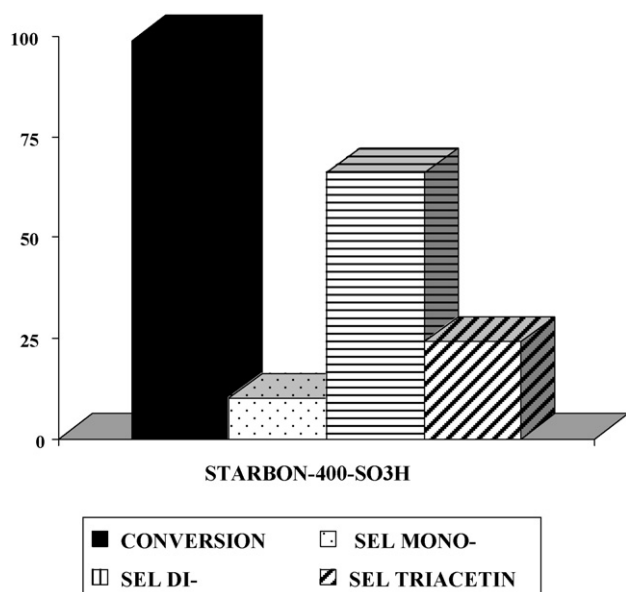


Fig. 2. Optimised preparation of diacetyl glycerol from the esterification of glycerol with acetic acid. Reaction conditions: 10 mmol glycerol, 30 mmol acetic acid, 300 W, 130 °C, 15 min, 0.2 g Starbon[®]-400-SO₃H.

ratios were found optimum for the production of di- (Fig. 2) and triacetyl glycerols (Fig. 3), respectively. Monoacetyl glycerol (mainly the 1-monoacetyl glycerol) was preferentially obtained at short times of reaction (<15 min) and low microwave powers (Fig. 1) whereas increasing catalyst quantities and maximum microwave power favoured the formation of 1,3-diacetyl glycerol (Fig. 2).

Only minor quantities of the 2-monoacetyl glycerol and 1,2-diacetyl glycerol were found. Longer reaction times combined with an increase in the amount of catalyst at maximum power provided improved selectivities to triacetin.

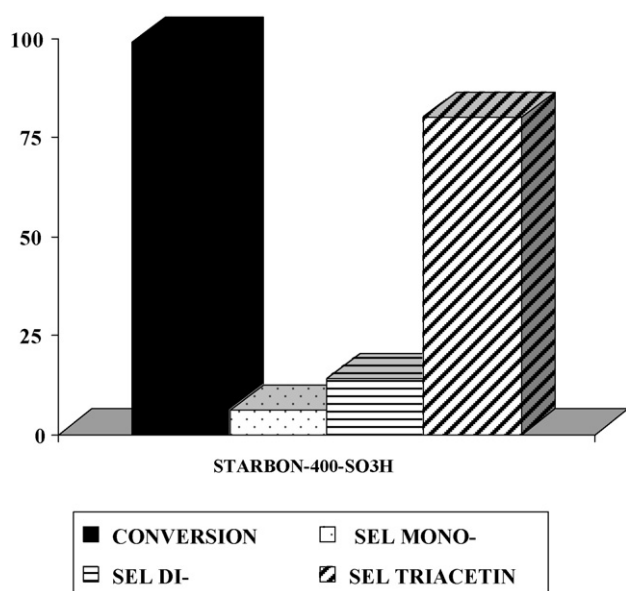


Fig. 3. Optimised preparation of triacetyl glycerol from the esterification of glycerol with acetic acid. Reaction conditions: 10 mmol glycerol, 60 mmol acetic acid, 300 W, 130 °C, 30 min, 0.2 g Starbon[®]-400-SO₃H.

Table 1

Catalytic activity of different solid acids tested in the esterification of glycerol with acetic acid^a

Entry	Catalyst	Conversion (mol%)	Selectivity monoester (mol%)	Selectivity diester (mol%)	Selectivity triester (mol%)
1	No catalyst	<10	50	40	10
2	H ₂ SO ₄	85	43	32	25
3	Sulphated zirconia	>90	15	37	48
4	Starbon [®] -400-SO ₃ H	>99	8	15	77

^a Reaction conditions: 10 mmol glycerol, 30 mmol acetic acid, microwave, 300 W, 130 °C, 30 min, 0.2 g catalyst.

Table 1 summarises the comparison of the activity of various catalysts in the esterification reaction. Under the same reaction conditions, the Starbon[®] acid was found to be the most active and selective catalyst.

No reports can be found on the acetylation of glycerol under microwave irradiation. Nevertheless, Table 2 summarises some of the main and optimised results on the reaction reported by different authors. Our Starbon[®] material provided improved conversion values with an unprecedented high selectivity to the mono- and diacetyl glycerols.

3.2. Glycerol etherification

The Starbon[®] acid was then tested in the etherification reaction of glycerol using a variety of aryl/alkyl alcohols. Preliminary results employing 1-phenyl-1-propanol as alcohol (under microwave irradiation) provided quantitative conversion and a mixture of monoether substituted compounds, mainly 1-phenyl-1-propyl-1-glyceryl ether (A) and 1-phenyl-1-propyl-2-glyceryl ether (B) in a short time (<5 min, Scheme 1) with a 12/1 A/B ratio as determined by ¹H NMR. Various substrates were tested in the etherification of glycerol, giving moderate to very good conversion and selectivities to the monoether (Table 3), using the Starbon[®]-400-SO₃H. The activity of the Starbon[®] acid was also compared to different solid acid catalysts (Table 4).

The Starbon[®] acid exhibited a similar activity to that of the silica sulphonated material and an improved performance compared to some other acid catalysts including beta zeolite and *para*-toluene sulfonic acid (*p*-TSA). A slightly improved selectivity to the monoether in the 1-position was also obtained with respect to the other solid acids tested in the etherification reaction. Interestingly, the formation of the monoether in the 2-position was more favoured in the case of the zeolite beta, a selectivity that can be attributed to shape selectivity issues within the microporous solid or a change in selectivity at low conversions. This selectivity switch was not observed in any of the other solid acids screened. Of note was also the presence of increasing quantities of diethers at longer reaction times (>20 min).

Comparative reported results with different catalysts for the particular example of *tert*-butyl alcohol have also been included in Table 5. The Starbon[®] acids provided quantitative conversion of glycerol and unique selectivities to monoethers with respect to the other reported solid acids.

Table 2

A comparison of the catalytic activity of different protocols and catalysts in the esterification of glycerol with acetic acid

Entry [ref.]	Reaction conditions	Conversion (mol%)	Selectivity monoester (mol%)	Selectivity diester (mol%)	Selectivity triester (mol%)
1 (Fig. 1)	Starbon [®] acid, mw, glycerol:HAc 1:1 ratio, mw, 100 W, 100 °C, 10 min, 0.1 g catalyst	>99	82	17	2
2 (Fig. 2)	Starbon [®] acid, mw, glycerol:HAc 1:3 ratio, mw, 300 W, 130 °C, 15 min, 0.2 g catalyst	>99	10	66	24
3 (Fig. 3)	Starbon [®] acid, glycerol:HAc 1:6 ratio, mw, 300 W, 130 °C, 30 min, 0.2 g catalyst	>99	6	14	80
4 [6]	Propylsulfonic acid SBA-15 supported, glycerol:HAc 1:9 ratio, 150 °C, 4 h, 0.2 g catalyst	70	7	48	43
5 [6]	Amberlyst-15, glycerol:HAc 1:9 ratio, 125 °C, 4 h, 0.2 g catalyst	83	<15	85 (di- + triester)	
6 [6]	Nafion SAC-13, glycerol:HAc 1:9 ratio, 125 °C, 4 h, 0.2 g catalyst	85	<20	83 (di- + triester)	
7 [25]	<i>p</i> -TSA-activated carbon, glycerol:HAc 1:4 ratio, 4 h, 130 °C, 0.1–0.2 g catalyst	>90	<5	<5	>90
8 [26]	Solid acid resin, glycerol:HAc 1:4.5 ratio, 5 h, 90–100 °C, 0.1 g catalyst	>90	<5	<5	>90

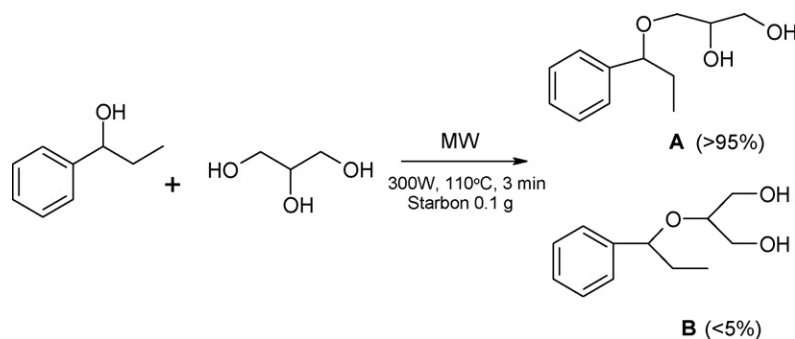
Scheme 1. Etherification of glycerol with 1-phenyl-1-propanol using Starbon[®]-400-SO₃H. Reaction conditions: 2 mmol glycerol, 6 mmol 1-phenyl-1-propanol, microwave, 300 W, 110 °C, 3 min, 0.1 g Starbon[®]-400-SO₃H.

Table 3

Catalytic activity of Starbon[®]-400-SO₃H in the etherification of glycerol with various substrates^a

Entry	Alcohol	Conversion (mol%)	Monoether-1/monoether-2 ratio (determined by ¹ H NMR)
1		>99	10/1
2	1-phenyl-1-propanol 	95	5/1
3	Benzyl alcohol 	87	1/1
4	Allylic alcohol 	74	3/1
5	3-Octen-1-ol 	66	8/1
	<i>tert</i> -butyl alcohol 		

^a Reaction conditions: 2 mmol glycerol, 6 mmol alcohol, microwave, 300 W, 110–140 °C, 15 min, 0.1 g catalyst.

Table 4

Catalytic activity of different solid acids tested in the etherification of glycerol with benzyl alcohol^a

Entry	Catalyst	Conversion (mol%)	Monoether-1/monoether-2 ratio (determined by ¹ H NMR)
1	No catalyst	–	–
2	Silica-SO ₃ H	>99	3/1
3	Starbon [®] -400-SO ₃ H	95	5/1
4	Zeolite beta-25	29	1/1
5	<i>p</i> -TSA	72	4/1

^aReaction conditions: 2 mmol glycerol, 6 mmol benzyl alcohol, microwave, 300 W, 110–120 °C, 15 min, 0.1 g catalyst.

Table 5

A comparison of the catalytic activity of Starbon[®]-400-SO₃H with different reported catalysts in the etherification of glycerol with *tert*-butyl alcohol

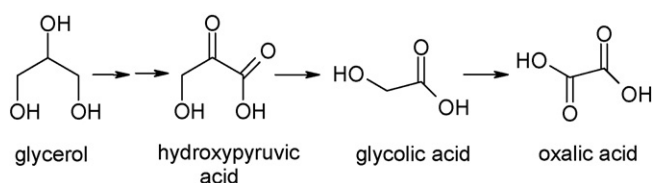
Entry [ref.]	Reaction conditions	Glycerol conversion (mol%)	Selectivity monoether (mol%)	Selectivity diether (mol%)	Selectivity triether + others (mol%)
1	Starbon [®] acid, glycerol: <i>tert</i> -butyl alcohol 1:3 ratio, mw, 300 W, 100–120 °C, 15 min, 0.1 g catalyst	66	>99	Traces	–
4 [27,28]	Amberlyst 15, glycerol: <i>tert</i> -butyl alcohol 1:4 ratio, 60–90 °C, 8 h, 0.38 g catalyst	>95	<20	>55	>25
5 [27,28]	Zeolite H-Y, glycerol: <i>tert</i> -butyl alcohol 1:4 ratio, 60–90 °C, 8 h, 0.38 g catalyst	>95	>15	>55	<30

3.3. Glycerol oxidation

The oxidation of glycerol with hydrogen peroxide (30%, v/v) under microwave irradiation employing a Starbon[®] supported Pd material (9.2% Pd) was then studied. The main products obtained in the oxidation of glycerol (glycolic acid and oxalic acid) are highlighted in Scheme 2.

Ketchie et al. have recently reported the formation of glycolic acid via C–C cleavage of the C₃ molecule in the presence of increasing concentrations of H₂O₂. [29] The presence of Pd in the catalyst seemed to have a strong influence on the selectivity of the reaction. Our results were in good agreement with theirs as we observed glycolic acid (hydroxyethanoic acid) as the main product at short times of reaction and low microwave powers (100 W, less than 15 min). Increasing quantities of oxalic acid were observed after further oxidation of glycolic acid at longer reaction times and increasing quantities of catalyst (>15–30 min). The results are summarised in Table 6. Several parameters were investigated in the oxidation reaction.

An increase in microwave power increased the glycerol conversion at the expense of the glycolic acid selectivity. However, the glycolic acid was still obtained in selectivities over 75%. Short reaction times (5–15 min) provided good to



Scheme 2. Products of reaction pathway in the oxidation of glycerol.

excellent conversions and selectivities to glycolic acid whilst oxalic acid was the major product found at longer times of reaction (>30 min). The quantity of catalyst employed in the reaction was found to have a similar effect to that of the time of reaction. Interestingly, no significant quantities of glyceric acid were found (<5%), supporting the fact that the reaction takes place through the oxidation of the secondary hydroxyl group, leading to glycolic acid in the first step and then to oxalic acid after further oxidation with H₂O₂ (Scheme 2). Prati and co-workers have also reported a similar behaviour on a Pd/C catalyst when increasing the temperature of reaction [18,30], but this is the first report of the production of glycolic and oxalic acids as major products.

Few reports can be found on the oxidation of glycerol with hydrogen peroxide. Hutchings and co-workers found formic acid and formate esters of glycerol as major products in the oxidation of glycerol with H₂O₂ using silicalite and aluminophosphate catalysts [31] but glycolic acid was also detected (>20% selectivity). The oxidation seemed to take place through oxidative cleavage of the C₃ intermediate (hydroxypyruvic acid) and resulted in the formation of glycolic and formic acid. Glycolic acid was then further oxidised to formic acid (does not decompose to CO₂), which reacts with some of the unconverted glycerol to give a glycerol ester. The oxidation of glycolic acid was favoured by a combination of conditions including the microporosity in the materials and the reactivity of the oxygen donor (H₂O₂) [31]. However, mesoporous materials in the presence of hydrogen peroxide as well as similar palladium supported catalysts (Pd/C) with molecular oxygen as oxygen donor were found to favour the partial oxidation products of glycerol, including glycolic, oxalic and formic acids [31–33].

Table 6

Catalytic activity of 9.2% Pd-Starbon[®]-400 tested in the oxidation of glycerol with hydrogen peroxide^a

Reaction conditions	Conversion (mol%)	Selectivity glycolic acid (mol%)	Selectivity oxalic acid (mol%)
No catalyst, 300 W, 100 °C, 30 min	<10	10 ^b	–
Effect of power			
100 W, 80 °C, 15 min, 0.1 g catalyst	70	90	<5
200 W, 85 °C, 15 min, 0.1 g catalyst	88	80	16
300 W, 100 °C, 15 min, 0.1 g catalyst	>95	75	22
Effect of time of reaction			
300 W, 100 °C, 5 min, 0.1 g catalyst	58	80	20
300 W, 100 °C, 15 min, 0.1 g catalyst	>95	75	22
300 W, 100 °C, 30 min, 0.1 g catalyst	>95	30	60
Effect of catalyst quantity			
300 W, 95 °C, 15 min, 0.05 g catalyst	62	80	15
300 W, 100 °C, 15 min, 0.1 g catalyst	>95	75	22
300 W, 110 °C, 15 min, 0.2 g catalyst	>95	35	55

The difference to 100 in selectivities is due to glyceric acid and tartronic acids.

^a Reaction conditions: 1 mmol glycerol, 4 mmol H₂O₂.^b Glyceric acid was obtained as major product.

Starbon[®] materials were reusable in all of the reactions (up to three times) preserving up to 85–90% of the initial catalytic activity, in good agreement with our results previously reported for the esterification of organic acids in water. [19–21] Selectivities were not significantly different on catalyst reuse confirming the high stability of the mesoporous carbonaceous materials.

4. Conclusions

Starbon[®] materials were successfully employed in a range of glycerol transformations confirming the versatility of the polysaccharide derived mesoporous solids in catalysis. They assisted the selective formation of various products including esters, ethers and acids under microwave irradiation.

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